Light-Scattering Investigations on the Liquid-Liquid Phase Transition in Ionic Solutions

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Coulomb interactions may drive a liquid-liquid phase transition in ionic solutions. Therefore, Ising criticality, usually found in separating fluids cannot be expected *a priori*, because of the long-range nature of the Coulomb interactions. Experimentally mean-field and Ising criticality [1] reported even for the same system.

For solutions of alkyl-ammonium picrates in higher alcohols Narayanan and Pitzer (NP) reported turbidity measurements which indicate a cross over from mean field to Ising criticality [2]. The Ising region was found to increase with the dielectric permittivity of the solvent. Unfortunately, we were not able to reproduce those results as in our experiments interference effects obscured the turbidity measurements in the region where cross over is expected.

In this work we report light scattering investigations on the systems investigated by NP. The scattering intensity is corrected for multiple scattering using the simulation method of Bailey and Cannell [3]. The temperature dependence of the single scattering intensity shows Ising-criticality and is well represented by the Ornstein-Zernike function. Deviations below temperatures $t \cong 0.01$ ($t = (T-Tc)/Tc$) are noticeable which may be described equally well by a constant background or corrections to scaling. In the high-temperature region our measurements essentially agree with the turbidity measurements of NP. The scaling analysis using a two-term Wegner expansion indicates a monotone cross over to mean-field criticality although in some cases the fit yields negative figures for the first correction term. In the case of the most polar alcohol (i-propanol) investigated the Ising region is definitely larger as in the cases of the higher alcohols. However, among those no trend relating the Wegner coefficients to the dielectric constant or the chain length of the alcohols can be established.

We also report light-scattering measurements and phase diagrams on ionic solutions in aprotic solvents (toluene, cyclohexane, chloroform). Ising criticality is established for those systems also. In variance to the findings on the alcohol solutions significant deviations from the Ornstein-Zernike function are not observable in the temperatur region $2\ 10^{-5} < t < 3\ 10^{-2}$.

[1] S. Wiegand, M.E. Briggs, J.M.H. Levelt Sengers, M. Kleemeier, and W. Schröer, *J. Chem. Phys*. **109**, 9038 (1998).
[2] T. Narayanan and K.S. Pitzer, *J. Chem. Phys*. **102**, 8118 (1995).
[3] A.E. Bailey and D.S. Cannell, *Phys. Rev. E* **50**, 4853 (1994).